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(54) **MULTILAYERED LAMINATED BODY**

(57) Abstract:

PROBLEM TO BE SOLVED: To obtain a multilayered laminated body, which is excellent in transparency, flexibility, heat sealing strength or the like and the transparency of which scarcely changes with time by a method wherein surface layer made of polypropylene-based resin is laminated onto one side of a base material layer consisting of polypropylene-based resin and specified hydrogenated diene- based polymer.

SOLUTION: The base material layer of this multilayered laminated body is made of resin composition C consisting of 95-20wt.% of polypropylene-based resin A and 5-80wt.% of hydrogenated diene-based polymer B, which is obtained by hydrogenating the double bond in the conjugated diene portion of at least one kind of polymer made mainly of the random copolymer portion between conjugated diene compound and aromatic vinyl compound. Onto one side of the base material layer, the surface layer made of resin composition D consisting of 100-50wt.% of the polypropylene-based resin A and 0-50wt.% of at least one kind of the hydrogenated diene polymer B, is laminated for obtaining the multilayered laminated body.

18-20, 22-35, 41-43, 45-57 58, 36 inherent 37-40 intended use 59-62

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[The technical field to which invention belongs] About a new multilayer layered product suitable as a film and a charge of a web material, this invention is excellent in transparency, flexibility, cold resistance, fusing seal intensity, heat-sealing intensity, etc. in more detail, and, moreover, relates to the small multilayer layered product of aging of transparency.
[0002]
[Description of the Prior Art] From the former, many monolayers or the multilayer film, and the charge of a web material are developed, and there is a Vinylon film as a typical film which is excellent in transparency, flexibility, feeling, etc. among such material. However, as for a Vinylon, the property top and feeling tend to receive influence in atmospheric temperature or humidity, and since especially cold resistance is bad, there is a limitation in use in the area and cold district where atmospheric temperature falls in winter. moreover, the fault that cost also cannot but become high since the producing-film method besides a remains acetic-acid smell or the problem of being easy to block is restricted to the solution cast method -- it is . In order to solve these troubles, much monolayers of a polyolefine system and multilayer film material are developed. The point that such polyolefine system material is inferior to a Vinylon film in transparency or flexibility although an improvement is found in respect of cost, cold resistance, etc. poses a problem. Furthermore, a recent-years and aromatic vinyl compound system polymer block, a conjugated-diene system compound polymer block, or a random-copolymer block with an aromatic vinyl compound and a conjugated-diene system compound, The hydrogenation diene system copolymer which hydrogenated the block copolymer which consists of two or more sorts of blocks of the taper block which consists of an aromatic vinyl compound and a conjugated-diene system compound, and an aromatic vinyl compound increases gradually, Generally carrying out [lamination] secondary elaboration to the sheet film which consists of a constituent which makes a polyolefine system resin a principal component is indicated (94 to open technical report 12864 reference). Moreover, it is indicated by carrying out the laminating of the resin which makes a propylene copolymer a principal component to the polyolefine film for retorts which carried out little combination of the hydrogenation block copolymer which becomes the polyolefine which makes a propylene ethylene block copolymer a subject from the polymer block which makes a subject an aromatic vinyl compound system polymer block and the hydrogenated conjugated-diene system compound that the film excellent in the balance of low-temperature impact resistance, transparency, retort resistance, and low-temperature heat-sealing nature is obtained (refer to JP,7-1662024,A). However, in the field of property balance where these films and sheets also synthesized aging of transparency in addition to transparency, flexibility, cold resistance, fusing seal intensity, and heat-sealing intensity, there is nothing on the level which can still be satisfied.
[0003]
[Problem(s) to be Solved by the Invention] this invention is made against the background of many problems of the above-mentioned conventional technology, and the technical problem is excellent in

transparency, flexibility, cold resistance, fusing seal intensity, heat-sealing intensity, etc., and is to offer the small multilayer layered product of aging of transparency moreover.
[0004]
[Means for Solving the Problem] Namely, this invention 95 - 20 % of the weight of polypropylene regin (b)s And a conjugated-diene compound To one [at least] field of the base-material layer formed from the resin constituent (c) which consists of 5 - 80 % of the weight of hydrogenation diene system polymer (b)s by which the double bond of the conjugated-diene portion of at least one sort of polymers made into a subject was hydrogenated, a random copolymerization portion with an aromatic vinyl compound Let the multilayer layered product which comes to carry out the laminating of the surface formed from the resin constituent (d) which consists of a polypropylene regin (b) of 100 - 50 % of the weight, and 0 - 50 % of the weight of at least one sort of hydrogenation diene system polymer (b)s be a summary.
[0005] Hereafter, this invention is explained in detail. Although you may be the copolymer of a propylene and other monomers even if the polypropylene regin used as a (b) component of a resin constituent (c) and a resin constituent (d) is well-known and it is a homopolymer, it is a copolymer preferably. As other desirable monomers in the aforementioned copolymer For example, ethylene; Butene-1, a pentene -1, a hexene -1, a heptene -1, the straight chain-like alpha olefin;4-methyl pentene - 1 of octene-1 grade, 2-methyl propene -1, 3-methyl pentene -1, 5-methyl hexene -1, 4-methyl hexene - 1 Four, The letter alpha olefin of branching of 4-dimethyl pentene-1 grade etc. is mentioned, it is ethylene; butene-1, a pentene -1, a hexene -1, a heptene -1, and the straight chain-like alpha olefin of octene-1 grade more preferably, and they are ethylene and butene-1 especially preferably. Other monomers of these are independent, or can mix and use two or more sorts. In this invention, by using the propylene system resin which consists of the aforementioned copolymer, the multilayer layered product excellent in physical-properties balance, such as transparency, flexibility, and cold resistance, is obtained, and the multilayer layered product excellent in especially the aforementioned physical-properties balance is obtained by using a propylene, ethylene, and/or a copolymer with butene-1 above all. the amount of copolymerization of other monomers in the aforementioned copolymer -- usually -- it is 2 - 10 % of the weight more preferably 12 or less % of the weight 15 or less % of the weight In this case, if there are more amounts of copolymerization of other monomers than 15 % of the weight, the improvement effect over the with-time fall of the transparency of the multilayer layered product obtained may become inadequate. Although there may be no limit especially about the structure of the aforementioned copolymer, for example, a random type, a block type, graft types, these hybrid models, etc. may be any, it is a random type preferably. Thus, by using the polypropylene regin which consists of a random type copolymer, the multilayer layered product excellent in especially physical-properties balance, such as transparency, flexibility, and cold resistance, is obtained. Although there is especially no limit as long as the melt flow rate (MFR:230 degree C, 2.16kg load) of a polypropylene regin can be fabricated as a film or a sheet, the multilayer layered product excellent in a moldability, transparency, etc. is preferably obtained for 10 minutes 0.5-15g / by considering as 1-10g / 10 minutes still more preferably. In this invention, the aforementioned polypropylene regin is independent, or two or more sorts can be mixed and used for it. The loadings of the polypropylene regin in a resin constituent (c) are 90 - 40 % of the weight especially preferably 90 to 30% of the weight preferably 95 to 20% of the weight. In this case, if there are more loadings of a polypropylene regin than 95 % of the weight, the flexibility and transparency of a film and a sheet will fall, and the intensity of the multilayer layered product obtained and the moldability of a constituent will fall at less than 20 % of the weight. Moreover, the loadings of the polypropylene regin in the resin constituent (d) of this invention are 95 - 85 % of the weight especially preferably 95 to 80% of the weight preferably 100 to 50% of the weight. In this case, although the loadings of a polypropylene regin are excellent in the transparency in early stages of a film and a sheet at less than 50 % of the weight, the fall of transparency with time becomes large.
[0006] next, (**) of resin constituent (**) and resin constituent (**) -- the hydrogenation diene system polymer used as a component consists of at least one sort of polymers which hydrogenated the polymer (henceforth "the polymer before hydrogenation") which makes a subject the random copolymerization portion of a conjugated-diene compound and an aromatic vinyl compound the polymerization before

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hydrogenation -- the content of a random copolymerization portion in the living body is 70 % of the weight or more especially preferably 60% of the weight or more still more preferably 50% of the weight or more preferably In this case, there is an inclination for the transparency of the multilayer layered product from which the content of this random copolymerization portion is obtained at less than 50 % of the weight, flexibility, cold resistance, etc. to fall. Moreover, in the polymer before hydrogenation, the rate of the sum total with 1 of the conjugated-diene unit in a random copolymerization portion, 2-combination, and 3 and 4-combination is 70% or more especially preferably 65% or more still more preferably 60% or more preferably to all conjugated-diene units. In this case, there is an inclination for the improvement effect over transparency and flexibility when the rate of the sum total with the above 1, 2-combination, and 3 and 4-combination blends with a polypropylene regin (b) at less than 60% to fall. In the polymer before hydrogenation as a conjugated-diene compound For example, 1,3-butadiene, an isoprene, 2, 3-dimethyl-1,3-butadiene, Although 1, 3-pentadiene, the 2-methyl -1, 3-pentadiene, 1, 3-hexadiene, 4, the 5-diethyl -1, 3-OKUTA diene, 3-butyl -1, 3-OKUTA diene, a chloroprene, etc. are mentioned In order to obtain the hydrogenation diene system polymer which could use industrially and was excellent in physical properties, 1,3-butadiene, isoprene, 1, and 3-pentadienes are 1,3-butadiene and an isoprene desirable especially preferably. These conjugated dienes are independent, or can mix and use two or more sorts. Moreover, as an aromatic vinyl compound, styrene, alpha-methylstyrene, p-methyl-styrene, t-butyl styrene, divinylbenzene, N, and N-dimethyl-p-aminoethyl styrene, N, and N-diethyl-p-aminoethyl styrene, a vinylpyridine, etc. are mentioned, for example, and they are styrene and an alpha methyl styrene preferably. These aromatic vinyl compounds are independent, or two or more sorts can be mixed and used for them. Although especially the weight ratio of the conjugated-diene compound / aromatic vinyl compound in the polymer before hydrogenation is not limited, they are 93 / 7 - 50/50 preferably [it is desirable and] to 95 / 5 - 40/60, and a pan.

[0007] Although the polymer before hydrogenation makes a subject the random copolymerization portion of a conjugated-diene compound and an aromatic vinyl compound, the polymer block like the following may be included by the case in the polymer chain. As the aforementioned polymer block, the polybutadiene block which makes a subject homopolymer block [of an aromatic vinyl compound], 1, and 4-combination, the taper-like polymer block which consists of a conjugated-diene compound and an aromatic vinyl compound, and an aromatic vinyl compound unit increases gradually are mentioned, for example. Although the feature on the physical properties of a hydrogenation diene system polymer falls a little when these polymer blocks exist in the chain of the polymer before hydrogenation, since it is dealt with when blocking nature falls and a sex improves, it may become advantageous industrially. the polymerization before hydrogenation -- although especially the content of the aforementioned polymer block in the living body is not limited, it is 30 or less % of the weight especially preferably 40 or less % of the weight still more preferably 50 or less % of the weight preferably In this case, when the content of a polymer block exceeds 50 % of the weight, there is an inclination for the transparency of the multilayer layered product obtained, flexibility, cold resistance, etc. to fall.

[0008] Moreover, the polymer before hydrogenation can also have the structure where the polymer chain extended or branched through the coupling-agent residue. In this case, as a coupling agent used, an adipic-acid diethyl, a divinylbenzene, a dimethyl chlorosilicane, a tetrachlorosilane, buthyl trichloro silicon, a dimethyldichlorosilane, tetrapod chloro tin, butyl TORIKURORO tin, tetrapod chloro germanium, 1, 2-dibromoethane, 1, 4-chloro methylbenzene, screw (trichlorosilyl) ethane, the epoxidation linseed oil, tolylene diisocyanate, 1 and 2, 4-benzene tri-isocyanate, etc. are mentioned, for example.

[0009] The double bond of a conjugated-diene portion [in / the polymer before hydrogenation / in a hydrogenation diene system polymer] is hydrogenated. On the occasion of this hydrogenation, the polymer before hydrogenation is independent, or two or more sorts can be mixed and used for it. The rate of hydrogenation in a hydrogenation diene system polymer is 90% or more especially preferably 85% or more still more preferably 80% or more preferably. In this case, there is an inclination for the transparency of a multilayer layered product, a mechanical strength, thermal resistance, weatherability, etc. to fall that the rate of hydrogenation is less than 80%. The polystyrene conversion number average

molecular weight (it is hereafter written as "number average molecular weight".) of a hydrogenation diene system polymer is 50,000-600,000 preferably [it is desirable and] to 50,000-700,000, and a pan. In this case, if a mechanical strength falls and 700,000 is exceeded when it becomes easy to block it less than by 50,000 when number average molecular weight pelletizes a hydrogenation diene system polymer, and it blends with a polypropylene regin (b), a fluidity, processability, etc. will fall. A hydrogenation diene system polymer can be manufactured by the method currently indicated by for example, the publication-number No. 72512 [three to] official report.

[0010] Furthermore, the hydrogenation diene system polymer used as a (b) component of a resin constituent (c) and a resin constituent (d) can also be a denaturation object which introduced one or more sorts of functional groups. As the aforementioned functional group, it is mentioned, for example, a carboxyl group, an acid-anhydride machine, a hydroxyl group, an epoxy group, the amino group, an ammonium-salt machine, a halogen atom content machine, a sulfonic group, etc. the basis guided from these functional groups, for example, an ester machine etc., etc. Such a functional group is introduced before the hydrogenation to the polymer before hydrogenation, or into the back according to those kinds. In this invention, the aforementioned hydrogenation diene system polymer is independent, or two or more sorts can be mixed and used for it.

[0011] The resin constituent (c) which forms the base-material layer of this invention consists of the aforementioned (b) component and a (b) component. The loadings of the (b) component in this resin constituent are 10 - 60 % of the weight especially preferably ten to 70% of the weight preferably five to 80% of the weight. In this case, at less than 5 % of the weight, the flexibility and transparency of a film and a sheet fall [the loadings of a (b) component], and if [than 80 % of the weight] more, the intensity and the moldability of a multilayer layered product which are obtained will fall. Moreover, the resin constituent (d) which forms the surface of this invention consists of a (b) component blended with the aforementioned (b) component by the case. The loadings of the (b) component in this resin constituent are 5 - 15 % of the weight especially preferably five to 20% of the weight preferably that what is necessary is just 50 or less % of the weight. In this case, if the loadings of a (b) component exceed 50 % of the weight, although the initial transparency of a film and a sheet is good, the fall of transparency with time becomes large. However, in this invention, it is desirable to make the loadings of the (b) component in a resin constituent (d) the loadings of the (b) component in a resin constituent (c) and below equivalent. The multilayer layered product which has the property which the multilayer layered product of this invention comes to carry out the laminating of the surface formed in one [at least] field of the base-material layer formed from a resin constituent (c) from a resin constituent (d), and the base-material layer and the surface compensated with it mutually in this multilayer layered product, or multiplied it, and was excellent is formed. Therefore, in this invention, terms and conditions, such as combination of the (b) component in a resin constituent (c) and a resin constituent (d) and a (b) component and loadings of a (b) component, are suitably selected according to the property of a request of a multilayer layered product. In this invention, it is the range which does not spoil the feature of this invention in essence, and the need is accepted. An ethylene propylene rubber (EPM), An ethylene-butene-1 copolymer (EBM), an ethylene-propylene-nonconjugated diene copolymer (EPDM), Olefin system (**) polymers, such as a polybutene -1 and polyethylene; An ionomer, Other resins, such as an ethylene vinylacetate copolymer (EVA), polyvinyl alcohol (PVA), and an ethylene-vinyl alcohol copolymer (EVOH), can also be blended into a resin constituent (c) and/or a resin constituent (d). Moreover, well-known additives, such as an organic system antimicrobial agent besides a blocking inhibitor, an antistatic agent, and lubricant, an inorganic system antimicrobial agent, an antioxidant, an antifogger, a coloring agent, and an ultraviolet ray absorbent, can also be blended with a resin constituent (c) and/or a resin constituent (d) in the range which does not spoil the feature of this invention in essence if needed. As the aforementioned blocking inhibitor, a silica, a zeolite, etc. may be suitable and any of nature and composition are sufficient as these, for example. Moreover, as the aforementioned antistatic agent, they are N which has the alkyl group of carbon numbers 12-18, and N-screw. -(2-hydroxyethyl)- Alkylamines and a glycerine fatty acid ester are desirable. Furthermore, as the aforementioned lubricant, a fatty-acid amide is desirable and an erucic-acid amide, a behenic acid

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amide, octadecanamide, oleic amide, etc. are specifically mentioned.
[0012] Although mixture with the (b) component and (b) component in the resin constituent (c) and the resin constituent (d) of this invention can be performed using proper mixers, such as a Banbury mixer, a roll mill, and an extrusion-molding machine, it is desirable to carry out melting kneading by the extrusion-molding in a plane, and it is desirable to carry out melting kneading especially using a biaxial extrusion-molding machine. Thus, by using the resin constituent which carried out melting kneading with the biaxial extrusion-molding machine, the fish eye in a film and a sheet decreases, and the film and sheet in which it not only excels in appearance, but transparency was further excellent are obtained. In addition, the resin constituent which carried out melting kneading using the biaxial extrusion-molding machine is used, usually pelletizing it. The multilayer layered product of this invention is (a). A base-material layer and a surface Tubular film process, After fabricating by the usual methods, such as a T die method, on a film or a sheet, The method and (b) which carry out heat pasting How to carry out direct laminate molding with co-extrusion type an inflation-molding machine and a T die extrusion-molding machine, (c) For example, the above By the method that the method of extruding and laminating the layer of another side in one [at least] field of the base-material layer beforehand fabricated by the method of (a) or a surface etc. is well-known, a laminating can be carried out and it can manufacture. Above (a) And (b) A multi-manifold type or feed block type any are sufficient as the T die of the T die extrusion-molding machine used for a method. (b) among these methods It is the way, desirable especially as for a desirable method, a method uses a co-extrusion type T die extrusion-molding machine. Above (b) Although a multilayer extrusion can be carried out and law can be adopted, the thing of four layers or more besides the two-layer co-extrusion method which carries out the laminating of the surface to one field of a base-material layer by the method, and the three-layer co-extrusion method which carries out the laminating of the surface to the field of both base-material layers done to the field of both base-material layers for the laminating of the surface at least from the point of aging of a blocking resistance and transparency is desirable. Moreover, although the multilayer layered product of this invention is used for the use as which transparency is required as both mirror planes, it may give designs, such as a mat, drawing, and mold push, to at least one side of the surface of an outermost layer of drum for the use as which transparency is not required so much. Even if each surface by which the laminating of the multilayer layered product of this invention was carried out to both sides of a base-material layer although the laminating of the surface was carried out to one field of a base-material layer or both fields is the same, it may differ, and it can also carry out the laminating of the surface to one field of a base-material layer, or both fields more than two-layer. The multilayer layered product of this invention can also be used pasting it together by two or more cases. Although the thickness of the multilayer layered product of this invention is suitably chosen according to the property and use of a request of a multilayer layered product, it is 20 micrometers or more from a viewpoint of a moldability and intensity that it is 10 micrometers or more desirable still more preferably. Moreover, although the ratio of the thickness of the base-material layer and surface in the multilayer layered product of this invention is suitably chosen according to the property and use of a request of a multilayer layered product, the range of a base-material layer / surface =2 / 1 - 6/1 is in the range of a base-material layer / surface =1 / 1 - 8/1 desirable still more preferably.
[0013]
[Embodiments of the Invention] Although an example is given and the gestalt of operation of this invention is explained still more concretely hereafter, this invention is not restrained at all by these examples, unless the summary is exceeded. Various evaluations in an example and the example of comparison were performed as follows.
It measured by absorption of the phenyl group of 679cm-1 by the amount (% of the weight) infrared analysis of combination of an aromatic vinyl compound.
It computed by the Hampton technique using the vinyl joint content (%) infrared analysis of a conjugated-diene portion.
A tetrachloroethylene is used as a rate (%) solvent of hydrogenation, and it is 100MHz. It computed by 1 H-NMR spectrum.

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It computed by having carried out polystyrene conversion by the gel permeation chromatography (GPC) in 135 degrees C, using a trichlorobenzene as a number-average-molecular-weight solvent of a hydrogenation diene system polymer.
Film intensity ASTM D Based on 882, film intensity was measured and it judged on the following criteria.
Film intensity is 300 kgf/cm2. Above ... O film intensity is 300 kgf/cm2. Following ... x transparency ASTM D Based on 1003, the film haze immediately after fabrication (%) was measured, and it judged on the following criteria.
[In the case of 40-micrometer film in thickness]
A haze is 2% or less. ... O haze is 3% or less more highly than 2%. ... A ** haze is higher than 3%. ... x
[the case of 100-micrometer film in thickness]
A haze is 3% or less. ... O haze is 4% or less more highly than 3%. ... A ** haze is higher than 4%. ... x flexibility ASTM D It is based on 882 and is Young's modulus. (kg/mm2) It measured and judged on the following criteria.
Young's modulus is two or less [30kg //mm]. ... O Young's modulus is two or less / 40kg //mm] more highly / mm / 30kg /than 2. ... ** Young's modulus is higher than 2 mm 40kg /. ... By x cold-resistant tactile feeling of -10 degrees C, it judged on the following criteria.
It is flexible on a par with the case of ordinary temperature. ... It compares with the case of O ordinary temperature, and is a stiff a little. ... It compares with the case of ** ordinary temperature, and is very a stiff. ... After performing x fusing seal on-the-strength fusing seal, the seal section was torn, and it judged on the following criteria.
The seal section is not destroyed but the non-seal section is extended. ... O Although the seal section splits, there is resistance and the non-seal section is also extended. ... There is no ** resistance, and the seal section splits. ... About the film haze (%) after leaving it for one week in the thermostat which is 50 degrees C of aging of x transparency, it is ASTMD. It measured based on 1003 and the following criteria estimated.
A difference with an initial haze is 0.5 or less. ... O A difference with an initial haze is 1.0 or less more greatly than 0.5. ... A difference with the initial haze of ** is larger than 1.0. ... Each component used for combination prescription of x example and the example of comparison is as follows.
(b) Component (I -1) Polypropylene (product [made from Chisso Petrochemistry], and tradename FM831B)
(**-2) Polypropylene (the Mitsubishi Chemical make, tradename FX4)
(b) Hydrogenation diene system polymer shown in the component table 1 (low 1) - (low 6) was compounded. Hydrogenation diene system polymer (low 7) It is a hydrogenation styrene [by Shell company]-butadiene-styrene block copolymer (SEBS) (tradename Clayton G-1652). The microstructure, the number average molecular weight, and the rate of hydrogenation of these hydrogenation diene system polymers are collectively shown in Table 1.
[0014]
[Example]
the example 1 (I -1) component 80 weight section and the component (low 1) 20 weight section -- the biaxial extrusion-molding machine by IKEGAI CORP. -- it pelletized, after carrying out melting kneading using PCM-45, and a resin constituent (c) was obtained Moreover, it pelletized, after carrying out melting kneading of the silica 0.2 weight section similarly as the component (I -1) 92.5 weight section, the component (low 1) 7.5 weight section, and a blocking inhibitor, and a resin constituent (d) was obtained. The extrusion-molding machine (:65mmphi modern machinery company make and for base-material layers, :50mmphi for surfaces) with which the three-layer film equipped with the T die with a feed block can fabricate each obtained resin constituent was supplied, the three-layer co-extrusion was performed as the extrusion temperature of 240 degrees C, and cooling roller temperature of 20 degrees C, and the ratio of 40 micrometers in thickness and the thickness of each class obtained the three-layer layered product of 1/4/1. Subsequently, various evaluations were performed after performing the usual aging. Consequently, the obtained three-layer layered product was excellent in transparency,

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flexibility, cold resistance, fusing seal intensity, and film intensity, and its aging of transparency was also very small. An evaluation result is shown in Table 2.
[0015] Various evaluations were performed like the example 1 except having used the component (I -2) instead of example 2 (I -1) component. Consequently, the obtained three-layer layered product was excellent in transparency, flexibility, cold resistance, fusing seal intensity, and film intensity, and its aging of transparency was also very small. An evaluation result is shown in Table 2.
[0016] Various evaluations were performed like the example 1 except having used the component (low 2) or (low 3) the component instead of example 3 and example 4 (low 1) component. Consequently, the obtained three-layer layered product was excellent in transparency, flexibility, cold resistance, fusing seal intensity, and film intensity, and its aging of transparency was also very small. An evaluation result is shown in Table 2.
[0017] The resin constituent (d) which consists of resin constituent (**) and (I -1) the component 85 weight section which consist of the component (I -1) 40 weight section and the component (low 1) 60 weight section, the component (low 1) 15 weight section, and the blocking inhibitor silica 0.2 weight section like example 5 example 1 was obtained. Subsequently, except having set thickness to 100 micrometers, various evaluations were performed, after obtaining a three-layer layered product from each obtained resin constituent like an example 1. Consequently, the obtained three-layer layered product was excellent in transparency, flexibility, cold resistance, and film intensity, and its aging of transparency was also very small. An evaluation result is shown in Table 2.
[0018] Except that the ratio of the thickness of a surface and a base-material layer obtained one fourth of two-layer layered products from the same resin constituent (c) as example 6 example 5, and a resin constituent (d), various evaluations were performed like the example 1. Consequently, the obtained two-layer layered product was excellent in transparency, flexibility, cold resistance, and film intensity. An evaluation result is shown in Table 2.
[0019] Instead of [of the examples 1-4 (low 1) of comparison] (low 4) Various evaluations were performed like the example 1 except having used - (low 7). Consequently, although the three-layer layered product of the example 1 of comparison was excellent in transparency, fusing seal intensity and film intensity were inferior, and blocking has not used aging of transparency as a garments material packing film violently greatly, either. The three-layer layered product of the examples 2-4 of comparison was still more opaque. An evaluation result is shown in Table 3.
[0020] Various evaluations were performed like the example 1 except having obtained a resin constituent (c) from the example of comparison 5 (I -1) component 98 weight section, and the component (low 1) 2 weight section. Consequently, transparency, flexibility, fusing seal intensity, etc. were inferior in the obtained three-layer layered product. An evaluation result is shown in Table 3.
[0021] Various evaluations were performed like the example 1 except having obtained a resin constituent (c) from the example of comparison 6 (I -1) component 10 weight section, and the component (low 1) 90 weight section. Consequently, film intensity was inferior in the obtained three-layer layered product. An evaluation result is shown in Table 3.
[0022] Various evaluations were performed like the example 1 except having obtained a resin constituent (d) from the example of comparison 7 (I -1) component 60 weight section, the component (low 1) 40 weight section, and the silica 0.2 weight section. Consequently, the obtained three-layer layered product had large aging of transparency. An evaluation result is shown in Table 3.
[0023]
[Table 1]

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表 1

水添ジエン系共重合体	ロ-1	ロ-2	ロ-3	ロ-4	ロ-5	ロ-6	ロ-7
水添前重合体の構造							
・共役ジエン化合物	BD(*1)	BD	BD	BD	BD	BD	BD
・芳香族ビニル化合物	ST(*1)	ST	ST	ST	ST	ST	ST
・ランダム共重合部分の含量（重量%）	92	94	85	94	94	92	0
・共役ジエン単位の1,2-結合と3,4-結合との合計の割合(*2)	82	79	78	75	20	78	−
・共役ジエン化合物／芳香族ビニル化合物の重量比	88／12	93／ 7	78／22	92／ 8	91／ 9	90／10	71／29
水素添加率（%）	99	99	97	97	95	30	99
数平均分子量（×10⁴）	31	39	28	4.5	25	76	−

(*1) BD：ブタジエン、ST：スチレン。
(*2) ランダム共重合部分における全共役ジエン単位に対する割合（%）。

[0024]
[Table 2]

表 2

	実施例					
	1	2	3	4	5	6
樹脂組成物（ハ）						
・（イ）成分（重量%）	イ-1 (80)	イ-2 (80)	イ-1 (80)	イ-1 (80)	イ-1 (40)	イ-1 (40)
・（ロ）成分（重量%）	ロ-1 (20)	ロ-1 (20)	ロ-2 (20)	ロ-3 (20)	ロ-1 (60)	ロ-1 (60)
樹脂組成物（ニ）						
・（イ）成分（重量%）	イ-1 (92.5)	イ-2 (92.5)	イ-1 (92.5)	イ-1 (92.5)	イ-1 (85)	イ-1 (85)
・（ロ）成分（重量%）	ロ-1 (7.5)	ロ-1 (7.5)	ロ-2 (7.5)	ロ-3 (7.5)	ロ-1 (15)	ロ-1 (15)
透明性	○	○	○	○	○	○
柔軟性	○	○	○	○	○	○
耐寒性	○	○	○	○	○	○
溶断シール強度	○	○	○	○	−	−
フィルム強度	○	○	○	○	○	○
透明性の経時変化	○	○	○	○	○	△

[0025]
[Table 3]

h g cg b eb cg e e

表 3

	比較例						
	1	2	3	4	5	6	7
樹脂組成物（ハ）							
・（イ）成分（重量%）	イ-1 (80)	イ-2 (80)	イ-1 (80)	イ-1 (80)	イ-1 (98)	イ-1 (10)	イ-1 (80)
・（ロ）成分（重量%）	ロ-4 (20)	ロ-5 (20)	ロ-6 (20)	ロ-7 (20)	ロ-1 (2)	ロ-1 (90)	ロ-1 (20)
樹脂組成物（ニ）							
・（イ）成分（重量%）	イ-1 (92.5)	イ-2 (92.5)	イ-1 (92.5)	イ-1 (92.5)	イ-1 (92.5)	イ-1 (92.5)	イ-1 (60)
・（ロ）成分（重量%）	ロ-4 (7.5)	ロ-5 (7.5)	ロ-6 (7.5)	ロ-7 (7.5)	ロ-1 (7.5)	ロ-1 (7.5)	ロ-1 (40)
透明性	○	×	×	×	×	○	○
柔軟性	○	△	△	△	×	○	○
耐寒性	○	−	−	−	△	○	○
溶断シール強度	×	−	−	−	×	○	○
フィルム強度	×	○	○	○	○	×	○
透明性の経時変化	×	−	−	−	○	○	×

[0026]
[Effect of the Invention] The multilayer layered product of this invention is excellent in transparency, flexibility, cold resistance, fusing seal intensity, heat-sealing intensity, etc., and moreover, its aging of transparency is small and can use it suitable for various fields, such as the film for garments material packing, a book jacket, the film for electronic-circuitry fabrication, the film for stationery packing, a medical-application packing film, a medical-application abandonment bag, medical hygienic goods, a makeup film, a surface-protection film, stationery, and a food container.

[Translation done.]

h g cg b eb cg e e

MULTILAYERED LAMINATED BODY

Patent Number: JP9254339
Publication date: 1997-09-30
Inventor(s): KODAMA KAZUHISA; FUJIMAKI KANAME; KAMISHINA JUNJI
Applicant(s): JAPAN SYNTHETIC RUBBER CO LTD
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EC Classification:
Equivalents:

Abstract

PROBLEM TO BE SOLVED: To obtain a multilayered laminated body, which is excellent in transparency, flexibility, heat sealing strength or the like and the transparency of which scarcely changes with time by a method wherein surface layer made of polypropylene-based resin is laminated onto one side of a base material layer consisting of polypropylene-based resin and specified hydrogenated diene- based polymer.
SOLUTION: The base material layer of this multilayered laminated body is made of resin composition C consisting of 95-20wt.% of polypropylene-based resin A and 5-80wt.% of hydrogenated diene-based polymer B, which is obtained by hydrogenating the double bond in the conjugated diene portion of at least one kind of polymer made mainly of the random copolymer portion between conjugated diene compound and aromatic vinyl compound. Onto one side of the base material layer, the surface layer made of resin composition D consisting of 100-50wt.% of the polypropylene-based resin A and 0-50wt.% of at least one kind of the hydrogenated diene polymer B, is laminated for obtaining the multilayered laminated body.

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(54)【発明の名称】　多層積層体

(57)【要約】

【課題】　透明性、柔軟性、耐寒性、溶断シール強度、ヒートシール強度等に優れ、しかも透明性の経時変化の小さい多層積層体を提供する。

【解決手段】　多層積層体は、ポリプロピレン系樹脂（イ）および共役ジエン化合物と芳香族ビニル化合物とのランダム共重合部分を主体とする重合体を水素添加した水添ジエン系重合体（ロ）からなる樹脂組成物（ハ）から形成された基材層の少なくとも片面に、上記（イ）成分を主体とする樹脂組成物（ニ）から形成された表層を積層してなる。

【特許請求の範囲】

【請求項１】　ポリプロピレン系樹脂（イ）９５～２０重量%および共役ジエン化合物と芳香族ビニル化合物とのランダム共重合部分を主体とする少なくとも１種の重合体の共役ジエン部分の二重結合が水素添加された水添ジエン系重合体（ロ）５～８０重量%からなる樹脂組成物（ハ）から形成された基材層の少なくとも一方の面に、ポリプロピレン系樹脂（イ）１００～５０重量%および少なくとも１種の水添ジエン系重合体（ロ）０～５０重量%からなる樹脂組成物（ニ）から形成された表層を積層してなる多層積層体。

【発明の詳細な説明】

【０００１】

【発明の属する技術分野】本発明はフィルムおよびシート材料として好適な新規多層積層体に関し、更に詳しくは透明性、柔軟性、耐寒性、溶断シール強度、ヒートシール強度等に優れ、しかも透明性の経時変化の小さい多層積層体に関する。

【０００２】

【従来の技術】従来から、数多くの単層あるいは多層のフィルムおよびシート材料が開発されており、このような材料のうち、透明性、柔軟性、風合い等に優れる代表的なフィルムとして、ビニロンフィルムがある。しかし、ビニロンはその特性上、風合いが気温や湿度に影響を受けやすく、特に耐寒性が悪いため、冬季に気温の下がる地域や寒冷地での使用には限界がある。また、残留酢酸臭やブロッキングしやすいという問題のほか、また製膜法が溶液キャスト法に限られるためコストも高くならざるを得ないという欠点のある。これらの問題点を解決するために、ポリオレフィン系の単層および多層のフィルム材料が多数開発されている。これらのポリオレフィン系材料は、コストおよび耐寒性等の面で改善がみられるものの、透明性や柔軟性がビニロンフィルムより劣る点が問題となっている。さらに近年、芳香族ビニル化合物系重合体ブロック、共役ジエン系化合物重合体ブロックもしくは芳香族ビニル化合物と共役ジエン系化合物とのランダム共重合体ブロック、芳香族ビニル化合物と共役ジエン系化合物からなり、芳香族ビニル化合物が漸増するテーパーブロックの２種以上のブロックより構成されるブロック共重合体を水素添加した水添ジエン系共重合体と、ポリオレフィン系樹脂とを主成分とする組成物からなるシート・フィルムに対して、ラミネート等の２次加工することが一般的に開示され（公開技報９４－１２８６４参照）、また、プロピレン・エチレンブロック共重合体を主体とするポリオレフィンに、芳香族ビニル化合物系重合体ブロックと水素添加された共役ジエン系化合物を主体とする重合体ブロックとからなる水添ブロック共重合体を少量配合したレトルト用ポリオレフィンフィルムに対して、プロピレン共重合体を主成分とする樹脂を積層することにより、低温耐衝撃性、透明性、

レトルト耐性および低温ヒートシール性のバランスに優れたフィルムが得られることが開示されている（特開平７－１６６２０２４号公報参照）。しかし、これらのフィルムおよびシートも、透明性、柔軟性、耐寒性、溶断シール強度およびヒートシール強度に加え、透明性の経時変化を総合した特性バランスの面では、未だ満足できるレベルにない。

【０００３】

【発明が解決しようとする課題】本発明は、上記従来技術の諸問題を背景になされたものであり、その課題は、透明性、柔軟性、耐寒性、溶断シール強度、ヒートシール強度等に優れ、しかも透明性の経時変化の小さい多層積層体を提供することにある。

【０００４】

【課題を解決するための手段】即ち、本発明は、ポリプロピレン系樹脂（イ）９５～２０重量%および共役ジエン化合物と芳香族ビニル化合物とのランダム共重合部分を主体とする少なくとも１種の重合体の共役ジエン部分の二重結合が水素添加された水添ジエン系重合体（ロ）５～８０重量%からなる樹脂組成物（ハ）から形成された基材層の少なくとも一方の面に、ポリプロピレン系樹脂（イ）１００～５０重量%および少なくとも１種の水添ジエン系重合体（ロ）０～５０重量%からなる樹脂組成物（ニ）から形成された表層を積層してなる多層積層体、を要旨とする。

【０００５】以下、本発明について詳細に説明する。樹脂組成物（ハ）および樹脂組成物（ニ）の（イ）成分として使用されるポリプロピレン系樹脂は公知のものであり、単独重合体であっても、プロピレンと他のモノマーとの共重合体であってもよいが、好ましくは共重合体である。前記共重合体における好ましい他のモノマーとしては、例えばエチレン；ブテン－１、ペンテン－１、ヘキセン－１、ヘプテン－１、オクテン－１等の直鎖状α－オレフィン；４－メチルペンテン－１、２－メチルプロペン－１、３－メチルペンテン－１、５－メチルヘキセン－１、４－メチルヘキセン－１、４，４－ジメチルペンテン－１等の分岐状α－オレフィン等が挙げられ、より好ましくはエチレン；ブテン－１、ペンテン－１、ヘキセン－１、ヘプテン－１、オクテン－１等の直鎖状α－オレフィンであり、特に好ましくは、エチレン、ブテン－１である。これらの他のモノマーは、単独でまたは２種以上を混合して使用することができる。本発明においては、前記共重合体からなるプロピレン系樹脂を使用することにより、透明性、柔軟性、耐寒性等の物性バランスに優れた多層積層体が得られ、就中プロピレンとエチレンおよび／またはブテン－１との共重合体を使用することにより、前記物性バランスに特に優れた多層積層体が得られる。前記共重合体における他のモノマーの共重合量は、通常、１５重量%以下、好ましくは１２重量%以下、より好ましくは２～１０重量%である。この

場合、他のモノマーの共重合量が１５重量%より多いと、得られる多層積層体の透明性の経時的低下に対する改良効果が不十分となる場合がある。前記共重合体の構造については特に制限がなく、例えばランダム型、ブロック型、グラフト型、これらの混合型等いずれであってもよいが、好ましくはランダム型である。このようにランダム型共重合体からなるポリプロピレン系樹脂を使用することにより、透明性、柔軟性、耐寒性等の物性バランスに特に優れた多層積層体が得られる。ポリプロピレン系樹脂のメルトフローレート（ＭＦＲ：２３０℃、２．１６ｋｇ荷重）は、フィルムあるいはシートとして成形可能である限り特に制限はないが、好ましくは０．５～１５ｇ／１０分、さらに好ましくは１～１０ｇ／１０分とすることにより、成形性、透明性等に優れた多層積層体が得られる。本発明において、前記ポリプロピレン系樹脂は、単独でまたは２種以上を混合して使用することができる。樹脂組成物（ハ）中のポリプロピレン系樹脂の配合量は、９５～２０重量%、好ましくは９０～３０重量%、特に好ましくは９０～４０重量%である。この場合、ポリプロピレン系樹脂の配合量が９５重量%より多いと、フィルムおよびシートの柔軟性および透明性が低下し、また２０重量%未満では、得られる多層積層体の強度および組成物の成形性が低下する。また、本発明の樹脂組成物（ニ）中のポリプロピレン系樹脂の配合量は、１００～５０重量%、好ましくは９５～８０重量%、特に好ましくは９５～８５重量%である。この場合、ポリプロピレン系樹脂の配合量が５０重量%未満では、フィルムおよびシートの初期の透明性には優れるが、経時的な透明性の低下が大きくなる。

【０００６】次に、樹脂組成物（ハ）および樹脂組成物（ニ）の（ロ）成分として使用される水添ジエン系重合体は、共役ジエン化合物と芳香族ビニル化合物とのランダム共重合部分を主体とする重合体（以下、「水添前重合体」という。）を水素添加した少なくとも１種の重合体からなる。水添前重合体中のランダム共重合部分の含量は、好ましくは５０重量%以上、さらに好ましくは６０重量%以上、特に好ましくは７０重量%以上である。この場合、該ランダム共重合部分の含量が５０重量%未満では、得られる多層積層体の透明性、柔軟性、耐寒性等が低下する傾向がある。また、水添前重合体において、ランダム共重合部分中の共役ジエン単位の１，２－結合と３，４－結合との合計の割合は、全共役ジエン単位に対して、好ましくは６０%以上、さらに好ましくは６５%以上、特に好ましくは７０%以上である。この場合、前記１，２－結合と３，４－結合との合計の割合が６０%未満では、ポリプロピレン系樹脂（イ）とブレンドした場合の透明性および柔軟性に対する改良効果が低下する傾向がある。水添前重合体において、共役ジエン化合物としては、例えば１，３－ブタジエン、イソプレン、２，３－ジメチル－１，３－ブタジエン、１，３－ペンタジエン、２－メチル－１，３－ペンタジエン、１，３－ヘキサジエン、４，５－ジエチル－１，３－オクタジエン、３－ブチル－１，３－オクタジエン、クロロプレン等が挙げられるが、工業的に利用でき、また物性の優れた水添ジエン系重合体を得るには、１，３－ブタジエン、イソプレン、１，３－ペンタジエンが好ましく、特に好ましくは１，３－ブタジエン、イソプレンである。これらの共役ジエンは、単独でまたは２種以上を混合して使用することができる。また、芳香族ビニル化合物としては、例えばスチレン、α－メチルスチレン、ｐ－メチルスチレン、ｔ－ブチルスチレン、ジビニルベンゼン、Ｎ，Ｎ－ジメチル－ｐ－アミノエチルスチレン、Ｎ，Ｎ－ジエチル－ｐ－アミノエチルスチレン、ビニルピリジン等が挙げられ、好ましくはスチレン、α－メチルスチレンである。これらの芳香族ビニル化合物は、単独でまたは２種以上を混合して使用することができる。水添前重合体における共役ジエン化合物／芳香族ビニル化合物の重量比は、特に限定されるものではないが、好ましくは９５／５～４０／６０、さらに好ましくは９３／７～５０／５０である。

【０００７】水添前重合体は、共役ジエン化合物と芳香族ビニル化合物とのランダム共重合部分を主体とするものであるが、場合により、その重合体分子鎖中に下記のごとき重合体ブロックが含まれていてもよい。前記重合体ブロックとしては、例えば、芳香族ビニル化合物の単独重合体ブロック、１，４－結合を主体とするポリブタジエンブロック、共役ジエン化合物と芳香族ビニル化合物からなり芳香族ビニル化合物単位が漸増するテーパー状重合体ブロック等が挙げられる。これらの重合体ブロックが水添前重合体の分子鎖中に存在することにより、水添ジエン系重合体の物性上の特徴は若干低下するものの、ブロッキング性が低下することにより取扱い性が向上するため、工業的に有利となる場合がある。水添前重合体中の前記重合体ブロックの含量は、特に限定されないが、好ましくは５０重量%以下、さらに好ましくは４０重量%以下、特に好ましくは３０重量%以下である。この場合、重合体ブロックの含量が５０重量%を超えると、得られる多層積層体の透明性、柔軟性、耐寒性等が低下する傾向がある。

【０００８】また、水添前重合体は、重合体分子鎖がカップリング剤残基を介して延長または分岐された構造を有することもできる。この場合に使用されるカップリング剤としては、例えばアジピン酸ジエチル、ジビニルベンゼン、ジメチルクロロシラン、四塩化ケイ素、ブチルトリクロロケイ素、ジメチルジクロロシラン、テトラクロロ錫、ブチルトリクロロ錫、テトラクロロゲルマニウム、１，２－ジブロムエタン、１，４－クロロメチルベンゼン、ビス（トリクロロシリル）エタン、エポキシ化アマニ油、トリレンジイソシアネート、１，２，４－ベンゼントリイソシアネート等が挙げられる。

【０００９】水添ジエン系重合体は、水添前重合体における共役ジエン部分の二重結合が水素添加されたものである。この水素添加に際して、水添前重合体は、単独でまたは２種以上を混合して使用することができる。水添ジエン系重合体における水素添加率は、好ましくは８０％以上、さらに好ましくは８５％以上、特に好ましくは９０％以上である。この場合、水素添加率が８０％未満であると、多層積層体の透明性、機械的強度、耐熱性、耐候性等が低下する傾向がある。水添ジエン系重合体のポリスチレン換算数平均分子量（以下、「数平均分子量」と略記する。）は、好ましくは５万～７０万、さらに好ましくは５万～６０万である。この場合、数平均分子量が５万未満では、水添ジエン系重合体をペレット化した場合ブロッキングしやすくなり、かつポリプロピレン系樹脂（イ）とブレンドした場合機械的強度が低下し、また７０万を超えると、流動性、加工性等が低下する。水添ジエン系重合体は、例えば特開平３―７２５１２号公報に開示されている方法によって製造することができる。

【００１０】さらに、樹脂組成物（ハ）および樹脂組成物（ニ）の（ロ）成分として使用される水添ジエン系重合体は、１種以上の官能基を導入した変性体であることもできる。前記官能基としては、例えばカルボキシル基、酸無水物基、水酸基、エポキシ基、アミノ基、アンモニウム塩基、ハロゲン原子含有基、スルホン酸基等や、これらの官能基から誘導される基、例えばエステル基等が挙げられる。このような官能基は、それらの種類に応じて、水添前重合体に対する水素添加の前または後に導入される。本発明において、前記水添ジエン系重合体は、単独でまたは２種以上を混合して使用することができる。

【００１１】本発明の基材層を形成する樹脂組成物（ハ）は、前記（イ）成分と（ロ）成分からなる。該樹脂組成物中の（ロ）成分の配合量は、５～８０重量%、好ましくは１０～７０重量%、特に好ましくは１０～６０重量%である。この場合、（ロ）成分の配合量が５重量%未満では、フィルムおよびシートの柔軟性および透明性が低下し、また８０重量%より多いと、得られる多層積層体の強度および成形性が低下する。また、本発明の表層を形成する樹脂組成物（ニ）は、前記（イ）成分と場合により配合される（ロ）成分からなる。該樹脂組成物中の（ロ）成分の配合量は、５０重量%以下であればよく、好ましくは５～２０重量%、特に好ましくは５～１５重量%である。この場合、（ロ）成分の配合量が５０重量%を超えると、フィルムおよびシートの初期透明性は良好であるが、経時的な透明性の低下が大きくなる。但し、本発明においては、樹脂組成物（ニ）中の（ロ）成分の配合量を、樹脂組成物（ハ）中の（ロ）成分の配合量と同等以下とすることが好ましい。本発明の多層積層体は、樹脂組成物（ハ）から形成される基材層の少なくとも一方の面に、樹脂組成物（ニ）から形成される表層を積層してなるものであり、かかる多層積層体においては、基材層と表層とが相互に補いあるいは相乗して、優れた特性を有する多層積層体が形成される。したがって本発明においては、樹脂組成物（ハ）および樹脂組成物（ニ）中の（イ）成分と（ロ）成分との組合せ、（ロ）成分の配合量等の諸条件は、多層積層体の所望の特性に応じて適宜選定される。本発明においては、本発明の特徴を本質的に損なわない範囲で、必要に応じてエチレン－プロピレン共重合体（ＥＰＭ）、エチレン－ブテン－１共重合体（ＥＢＭ）、エチレン－プロピレン－非共役ジエン共重合体（ＥＰＤＭ）、ポリブテン－１、ポリエチレン等のオレフィン系（共）重合体；アイオノマー、エチレン－酢酸ビニル共重合体（ＥＶＡ）、ポリビニルアルコール（ＰＶＡ）、エチレン－ビニルアルコール共重合体（ＥＶＯＨ）等の他の樹脂を、樹脂組成物（ハ）および／または樹脂組成物（ニ）中に配合することもできる。また、樹脂組成物（ハ）および／または樹脂組成物（ニ）には、本発明の特徴を本質的に損なわない範囲で、必要に応じてブロッキング防止剤、帯電防止剤、滑剤のほか、有機系抗菌剤、無機系抗菌剤、酸化防止剤、防曇剤、着色剤、紫外線吸収剤等の公知の添加剤を配合することもできる。前記ブロッキング防止剤としては、例えばシリカ、ゼオライト等が好適であり、これらは天然、合成の何れでもよい。また前記帯電防止剤としては、炭素数１２～１８のアルキル基を有するＮ，Ｎ－ビス－（２－ヒドロキシエチル）－アルキルアミン類やグリセリン脂肪酸エステルが好ましい。さらに、前記滑剤としては、脂肪酸アミドが好ましく、具体的にはエルカ酸アミド、ベヘニン酸アミド、ステアリン酸アミド、オレイン酸アミド等が挙げられる。

【００１２】本発明の樹脂組成物（ハ）および樹脂組成物（ニ）における（イ）成分と（ロ）成分との混合は、例えばバンバリーミキサー、ロールミル、押出し成形機等の適宜の混合機を用いて行うことができるが、押出し成形機中で溶融混練することが好ましく、特に２軸押出し成形機を用いて溶融混練することが好ましい。このように２軸押出し成形機により溶融混練した樹脂組成物を使用することにより、フィルムおよびシート中のフィッシュアイが少なくなり、外観に優れるばかりでなく、透明性がさらに優れたフィルムおよびシートが得られる。なお、２軸押出し成形機を用いて溶融混練した樹脂組成物は、通常、ペレット化して使用される。本発明の多層積層体は、例えば(a) 基材層と表層とをインフレーション法、Ｔダイ法等の通常の方法でフィルムあるいはシートに成形したのち、熱貼合する方法、(b) 共押出しタイプのインフレーション成形機やＴダイ押出し成形機により直接積層成形する方法、（ｃ）例えば前記 (a)の方法で予め成形した基材層あるいは表層の少なくとも一方の面に他方の層を押出しラミネートする方法等の公知の方

法で積層して製造することができる。前記(a) および(b) の方法に使用されるＴダイ押出し成形機のＴダイは、マルチマニホールドタイプまたはフィードブロックタイプの何れでもよい。これらの方法のうち、(b) の方法が好ましく、特に好ましい方法は、共押出しタイプのＴダイ押出し成形機を用いる方法である。前記(b) の方法では、基材層の一方の面に表層を積層する２層共押出し法、基材層の両方の面に表層を積層する３層共押出し法のほか、４層以上の多層押出し法を採用することができるが、耐ブロッキング性および透明性の経時変化の点から、少なくとも基材層の両方の面に表層を積層することが好ましい。また、本発明の多層積層体は、透明性が要求される用途には両鏡面として使用されるが、透明性がそれほど要求されない用途では、最外層の表層の少なくとも一方にマット、絞り、型押し等の意匠を施してもよい。本発明の多層積層体は、基材層の一方の面または両方の面に表層が積層されているが、基材層の両面に積層された各表層は同一でも異なってもよく、また基材層の一方の面または両方の面に、表層を２層以上積層することもできる。本発明の多層積層体は、場合により２つ以上貼合して使用することもできる。本発明の多層積層体の厚さは、多層積層体の所望の特性や用途に応じて適宜選択されるが、成形性および強度の観点から、１０μｍ以上であることが好ましく、さらに好ましくは２０μｍ以上である。また、本発明の多層積層体における基材層と表層との厚さの比率は、多層積層体の所望の特性や用途に応じて適宜選択されるが、基材層／表層＝１／１～８／１の範囲にあるのが好ましく、さらに好ましくは基材層／表層＝２／１～６／１の範囲である。

【００１３】

【発明の実施の形態】以下、実施例を挙げて本発明の実施の形態をさらに具体的に説明するが、本発明は、その要旨を超えない限り、これらの実施例に何ら制約されるものではない。実施例および比較例中の各種評価は、次のようにして行った。

<u>芳香族ビニル化合物の結合量（重量%）</u>

赤外分析法による６７９cm^{-1}のフェニル基の吸収により測定した。

<u>共役ジエン部分のビニル結合含量（%）</u>

赤外分析法を用い、ハンプトン法により算出した。

<u>水素添加率（%）</u>

溶媒として四塩化エチレンを用い、１００ＭＨｚでの^{1}Ｈ—ＮＭＲスペクトルにより算出した。

<u>水添ジエン系重合体の数平均分子量</u>

溶媒としてトリクロルベンゼンを用い、１３５℃におけるゲルパーミエーションクロマトグラフィー（ＧＰＣ）により、ポリスチレン換算して算出した。

<u>フィルム強度</u>

ＡＳＴＭ　Ｄ　８８２に準拠して、フィルム強度を測定し、以下の基準で判定した。

フィルム強度が３００kgf/cm^2 以上　・・・　○
フィルム強度が３００kgf/cm^2 未満　・・・　×

<u>透明性</u>

ＡＳＴＭ　Ｄ　１００３に準拠して、成形直後のフィルムヘーズ（%）を測定し、以下の基準で判定した。

〔厚さ４０μｍフィルムの場合〕
ヘーズが２%以下　・・・　○
ヘーズが２%より高く３%以下　・・・　△
ヘーズが３%より高い　・・・　×
〔厚さ１００μｍフィルムの場合〕
ヘーズが３%以下　・・・　○
ヘーズが３%より高く４%以下　・・・　△
ヘーズが４%より高い　・・・　×

<u>柔軟性</u>

ＡＳＴＭ　Ｄ　８８２に準拠して、ヤング率（kg/mm^2）を測定し、以下の基準で判定した。

ヤング率が３０kg/mm^2 以下　・・・　○
ヤング率が３０kg/mm^2 より高く４０kg/mm^2 以下　・・・　△
ヤング率が４０kg/mm^2 より高い　・・・　×

<u>耐寒性</u>

－１０℃における触感により、以下の基準で判定した。

常温の場合と同等に柔軟である　・・・　○
常温の場合に比べてやや硬い　・・・　△
常温の場合に比べて非常に硬い　・・・　×

<u>透明性の経時変化</u>

５０℃の恒温槽中に１週間放置したのちのフィルムヘーズ（%）を、ＡＳＴＭＤ　１００３に準拠して測定し、以下の基準で評価した。

初期ヘーズとの差が０．５以下　・・・　○
初期ヘーズとの差が０．５より大きく１．０以下　・・・　△
初期ヘーズとの差が１．０より大きい　・・・　×

<u>溶断シール強度</u>

溶断シールを行ったのちシール部を引裂き、以下の基準で判定した。

シール部は破壊せず非シール部が伸びる　・・・　○
シール部は裂けるが抵抗があり非シール部も伸びる　・・・　△
抵抗が無くシール部が裂ける　・・・　×

実施例および比較例の配合処方に用いた各成分は、以下の通りである。

（イ）成分

（イ-1）ポリプロピレン（チッソ石油化学（株）製、商

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品名ＦＭ８３１Ｂ）
（イ-2）ポリプロピレン（三菱化学（株）製、商品名ＦＸ４）
（ロ）成分
表１に示す水添ジエン系重合体（ロ-1）～（ロ-6）を合成した。水添ジエン系重合体（ロ-7）は、シェル（株）社製水添スチレン－ブタジエン－スチレンブロック共重合体（ＳＥＢＳ）（商品名クレイトンＧ－１６５２）である。これらの水添ジエン系重合体のミクロ構造、数平均分子量および水素添加率を、表１にまとめて示す。

【００１４】
【実施例】
実施例１
（イ-1）成分８０重量部と（ロ-1）成分２０重量部とを、（株）池貝製２軸押出し成形機ＰＣＭ－４５を用いて溶融混練りしたのちペレット化し、樹脂組成物（ハ）を得た。また、同様にして（イ-1）成分９２．５重量部、（ロ-1）成分７．５重量部およびブロッキング防止剤としてシリカ０．２重量部を溶融混練したのちペレット化し、樹脂組成物（ニ）を得た。得られた各樹脂組成物を、フィードブロック付きＴダイを備えた３層フィルムが成形可能な押出し成形機（モダンマシナリー社製、基材層用：６５ｍｍφ、表層用：５０ｍｍφ）に供給し、押出し温度２４０℃、冷却ロール温度２０℃として３層共押出しを行い、厚さ４０μｍ、各層の厚さの比率が１／４／１の３層積層体を得た。次いで、通常のエージングを行ったのち、各種評価を行った。その結果、得られた３層積層体は透明性、柔軟性、耐寒性、溶断シール強度およびフィルム強度が優れ、また透明性の経時変化も極めて小さいものであった。評価結果を表２に示す。

【００１５】実施例２
（イ-1）成分の代わりに（イ-2）成分を使用した以外は、実施例１と同様にして、各種評価を行った。その結果、得られた３層積層体は、透明性、柔軟性、耐寒性、溶断シール強度およびフィルム強度が優れ、また透明性の経時変化も極めて小さいものであった。評価結果を表２に示す。

【００１６】実施例３および実施例４
（ロ-1）成分の代わりに（ロ-2）成分または（ロ-3）成分を使用した以外は、実施例１と同様にして、各種評価を行った。その結果、得られた３層積層体は、透明性、柔軟性、耐寒性、溶断シール強度およびフィルム強度が優れ、また透明性の経時変化も極めて小さいものであった。評価結果を表２に示す。

【００１７】実施例５

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実施例１と同様にして、（イ-1）成分４０重量部と（ロ-1）成分６０重量部からなる樹脂組成物（ハ）および（イ-1）成分８５重量部と（ロ-1）成分１５重量部およびブロッキング防止剤シリカ０．２重量部からなる樹脂組成物（ニ）を得た。次いで、厚さを１００μｍとした以外は実施例１と同様にして、得られた各樹脂組成物から３層積層体を得たのち、各種評価を行った。その結果、得られた３層積層体は、透明性、柔軟性、耐寒性およびフィルム強度が優れ、また透明性の経時変化も極めて小さいものであった。評価結果を表２に示す。

【００１８】実施例６
実施例５と同様の樹脂組成物（ハ）および樹脂組成物（ニ）から、表層と基材層との厚さの比率が１／４の２層積層体を得た以外は、実施例１と同様にして、各種評価を行った。その結果、得られた２層積層体は、透明性、柔軟性、耐寒性およびフィルム強度が優れたものであった。評価結果を表２に示す。

【００１９】比較例１～４
（ロ-1）の代わりに（ロ-4）～（ロ-7）を使用した以外は、実施例１と同様にして、各種評価を行った。その結果、比較例１の３層積層体は、透明性に優れるものの、溶断シール強度およびフィルム強度が劣り、透明性の経時変化も大きく、またブロッキングが激しく衣料材料包装フィルムとして使用できなかった。さらに比較例２～４の３層積層体は、不透明であった。評価結果を表３に示す。

【００２０】比較例５
（イ-1）成分９８重量部と（ロ-1）成分２重量部から樹脂組成物（ハ）を得た以外は、実施例１と同様にして、各種評価を行った。その結果、得られた３層積層体は、透明性、柔軟性、溶断シール強度等が劣っていた。評価結果を表３に示す。

【００２１】比較例６
（イ-1）成分１０重量部と（ロ-1）成分９０重量部から樹脂組成物（ハ）を得た以外は、実施例１と同様にして、各種評価を行った。その結果、得られた３層積層体は、フィルム強度が劣っていた。評価結果を表３に示す。

【００２２】比較例７
（イ-1）成分６０重量部、（ロ-1）成分４０重量部およびシリカ０．２重量部から樹脂組成物（ニ）を得た以外は、実施例１と同様にして、各種評価を行った。その結果、得られた３層積層体は、透明性の経時変化が大きかった。評価結果を表３に示す。

【００２３】
【表１】

表 1

水添ジエン系共重合体	ロ-1	ロ-2	ロ-3	ロ-4	ロ-5	ロ-6	ロ-7
水添前重合体の構造							
・共役ジエン化合物	BD(*1)	BD	BD	BD	BD	BD	BD
・芳香族ビニル化合物	ST(*1)	ST	ST	ST	ST	ST	ST
・ランダム共重合部分の含量（重量%）	92	94	85	94	94	92	0
・共役ジエン単位の1,2-結合と3,4-結合との合計の割合(*2)	82	79	78	75	20	78	－
・共役ジエン化合物／芳香族ビニル化合物の重量比	88／12	93／7	78／22	92／8	91／9	90／10	71／29
水素添加率（%）	99	99	97	97	95	30	99
数平均分子量（$\times 10^4$）	31	39	28	4.5	25	76	－

(*1) BD：ブタジエン、ST：スチレン。
(*2) ランダム共重合部分における全共役ジエン単位に対する割合（%）。

【表2】

【0024】

表 2

	実施例					
	1	2	3	4	5	6
樹脂組成物（ハ）						
・（イ）成分（重量%）	イ-1 (80)	イ-2 (80)	イ-1 (80)	イ-1 (80)	イ-1 (40)	イ-1 (40)
・（ロ）成分（重量%）	ロ-1 (20)	ロ-1 (20)	ロ-2 (20)	ロ-3 (20)	ロ-1 (60)	ロ-1 (60)
樹脂組成物（ニ）						
・（イ）成分（重量%）	イ-1 (92.5)	イ-2 (92.5)	イ-1 (92.5)	イ-1 (92.5)	イ-1 (85)	イ-1 (85)
・（ロ）成分（重量%）	ロ-1 (7.5)	ロ-1 (7.5)	ロ-2 (7.5)	ロ-3 (7.5)	ロ-1 (15)	ロ-1 (15)
透明性	○	○	○	○	○	○
柔軟性	○	○	○	○	○	○
耐寒性	○	○	○	○	○	○
溶断シール強度	○	○	○	○	－	－
フィルム強度	○	○	○	○	○	○
透明性の経時変化	○	○	○	○	○	△

【表3】

【0025】

表 3

	比較例						
	1	2	3	4	5	6	7
樹脂組成物（ハ）							
・（イ）成分（重量%）	イ-1 (80)	イ-2 (80)	イ-1 (80)	イ-1 (80)	イ-1 (98)	イ-1 (10)	イ-1 (80)
・（ロ）成分（重量%）	ロ-4 (20)	ロ-5 (20)	ロ-6 (20)	ロ-7 (20)	ロ-1 (2)	ロ-1 (90)	ロ-1 (20)
樹脂組成物（ニ）							
・（イ）成分（重量%）	イ-1 (92.5)	イ-2 (92.5)	イ-1 (92.5)	イ-1 (92.5)	イ-1 (92.5)	イ-1 (92.5)	イ-1 (60)
・（ロ）成分（重量%）	ロ-4 (7.5)	ロ-5 (7.5)	ロ-6 (7.5)	ロ-7 (7.5)	ロ-1 (7.5)	ロ-1 (7.5)	ロ-1 (40)
透明性	○	×	×	×	×	○	○
柔軟性	○	△	△	△	×	○	○
耐寒性	○	−	−	−	△	○	○
溶断シール強度	×	−	−	−	×	○	○
フィルム強度	×	○	○	○	○	×	○
透明性の経時変化	×	−	−	−	○	○	×

【００２６】

【発明の効果】本発明の多層積層体は、透明性、柔軟性、耐寒性、溶断シール強度、ヒートシール強度等に優れ、しかも透明性の経時変化が小さく、衣料材料包装用フィルム、ブックカバー、電子回路成形用フィルム、文具包装用フィルム、医療用包装フィルム、医療用廃棄袋、医療衛生材料、化粧フィルム、表面保護フィルム、文具、食品容器等の様々な分野に好適に用いることができる。

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MULTILAYER LAMINATE
[多層積層体]

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(57) [Abstract]

[Problems to be Solved by the Invention]

The invention provides a multilayer laminate that is superior in transparency, flexibility, cold resistance, weld seal strength, heat seal intensity, etc.; furthermore, it provides a multilayer laminate where change of transparency over time is small.

[Means to Solve the Problems]

Multilayer laminate becomes, polypropylene resin (J2) and laminating surface layer where the substrate layer which was formed from resin composition (a) which consists of hydrogenated diene-based polymer (b) which polymer which designates random copolymer portion of conjugated diene compound and the aromatic vinyl compound as main component hydrogenated is done at least in one surface, was formed from resin composition (d) which designates above-mentioned (J2) component as the main component.

[Claim(s)]

[Claim 1]

Polypropylene resin (J2) 95 - 20 weight% and double bond of conjugated diene portion of polymer of at least 1 kind which designates random copolymer portion of conjugated diene compound and aromatic vinyl compound as the main component hydrogenated diene-based polymer which is done (b) on aspect of at least one of substrate layer which was formed from resin composition (a) which consists of 5 - 80 weight%, polypropylene resin (J2) 100 - 50 weight% and hydrogenated diene-based polymer of at least 1 kind (b) laminating surface layer which was formed from resin composition (d) which consists of 0 - 50 weight%, multilayer laminate which becomes.

[Description of the Invention]

[0001]

[Technological Field of Invention]

This invention regards preferred novel multilayer laminate as film and sheet material, furthermore details are superior in transparency, flexibility, cold resistance, weld seal strength, heat seal intensity, etc., furthermore, regard multilayer laminate where change in transparency over time is small.

[0002]

[Prior Art]

From until recently, many monolayer or film and sheet material of the multilayer to be developed, there is a vinylon film among this kind of material, as representative film which is superior in transparency, flexibility, texture, etc.

But because vinylon on characteristic, texture is easy to receive influence to gas temperature and humidity, especially cold resistance is bad, there is a limit in use with region and cold region where gas temperature goes down to Winter.

In addition, because other than problem that, in addition film production method is limited to solution casting method, remains acetic acid odor and blocking it is easy to do, either cost must become high, there is a deficiency.

In order to solve these problem, monolayer of polyolefin type and film material of multilayer are developed large number.

As for these polyolefin type materials, although you can see improvement in cost and cold resistance or other aspect, transparency and flexibility point which is inferior have become problem from vinylon film.

Furthermore, recently, it consists of random copolymer block, aromatic vinyl compound and conjugated diene compound of the aromatic vinyl compound polymer block, conjugated diene compound polymer block or aromatic vinyl compound and conjugated diene compound, laminating or other secondary it processes aromatic vinyl compound is formed vis-à-vis sheet * film which consists of hydrogenated diene-based copolymer which block copolymer which hydrogenated is done and composition which designates polyolefin resin as main component from block of 2 kinds or more of the taper block which crescendo is done, generally to be disclosed, (Kokai Giho 94-12864 reference), in addition, In polyolefin which designates propylene or ethylene block copolymer as main component, film which is superior in balance of low temperature impact resistance, transparency, retort resistance and low temperature heat seal property by laminating the resin which designates propylene copolymer as main component aromatic vinyl compound polymer block and vis-à-vis polyolefin film for retort which hydrogenated block copolymer which consists of polymer block which designates conjugated diene compound which hydrogenated is done as the main component trace is combined, is disclosed is acquired, (Japan Unexamined Patent Publication Hei 7-1662024 disclosure reference) .

But these film or sheet, in aspect of characteristic balance which synthesizes change in transparency over time in addition to transparency, flexibility, cold resistance, weld seal strength and heat seal intensity, there is not a level which still it can be satisfied.

[0003]

[Problems to be Solved by the Invention]

As for this invention, problem of above-mentioned Prior Art being something which can be made background, problem is superior in the transparency, flexibility, cold resistance, weld seal strength, heat seal intensity etc, furthermore, it is to offer multilayer laminate where change over time of the transparency is small.

[0004]

[Means to Solve the Problems]

Namely, as for this invention, polypropylene resin (J2) 95 - 20 weight% and double bond of conjugated diene portion of polymer of at least 1 kind which designates random copolymer portion of the conjugated diene compound and aromatic vinyl compound as main component hydrogenated diene-based polymer which is done (b) on aspect of at least one of substrate layer which was formed from the resin composition (a) which consists of 5 - 80 weight%, polypropylene resin (J2) 100 - 50 weight% and hydrogenated diene-based polymer of at least 1 kind (b) laminating surface layer which was formed from resin composition (d) which consists of 0 - 50 weight%, it designates multilayer laminate, which becomes as gist.

[0005]

You explain in detail below, concerning this invention.

Polypropylene resin which is used resin composition (a) and as (J2) component of resin composition (d) with those of public knowledge, even with homopolymer, is good even with the copolymer of propylene and other monomer, but it

is a preferably copolymer.

for example ethylene; butene-1, pentene-1, hexene-1, heptene-1, octene-1 or other straight chain α-olefin; 4-methylpentene-1,2-methyl propene-1,3-methylpentene-1,5-methyl hexene-1, 4- methyl hexene-1,4,4-dimethyl you can list pentene-1 or other branched α-olefin, etc., as desirable other monomer in aforementioned copolymer, with the more preferably ethylene; butene-1, pentene-1, hexene-1, heptene-1, octene-1 or other straight chain α-olefin, it is a particularly preferably, ethylene, butene-1.

Mixing alone or 2 kinds or more, you can use these other monomer.

Regarding to this invention, multilayer laminate which is superior in transparency, flexibility, cold resistance or other property balance by using propylene type resin which consists of aforementioned copolymer, is acquired, multilayer laminate which especially is superior in aforementioned property balance by especially using copolymer of ethylene and propylene and/or butene-1, is acquired.

Amount of copolymerization of other monomer in aforementioned copolymer, usually, 15 weight% or less, preferably 12 weight% or less, is more preferably 2 - 10 weight%.

In this case, when amount of copolymerization of other monomer is more than 15 weight%, there are times when improvement effect for decrease over time of transparency of multilayer laminate which is acquired becomes insufficient.

Concerning structure of aforementioned copolymer there is not especially restriction, is good whichever such as these mixed type of the, for example, random, block, graft, but it is a preferably random.

This way multilayer laminate which especially is superior in transparency, flexibility, cold resistance or other property balance by using polypropylene resin which consists of random copolymer, is acquired.

If melt flow rate (MFR: 230°C, 2.16 kg load) of polypropylene resin is formable as film or sheet, there is not especially restriction. multilayer laminate which is superior in moldability, transparency, etc., preferably 0.5 - 15 g/10 min, furthermore, by making preferably 1 - 10 g/10 min, is acquired.

Regarding to this invention, mixing alone or 2 kinds or more, you can use the aforementioned polypropylene resin.

Blended amount of polypropylene resin in resin composition (a) is 95 - 20 weight%, preferably 90 - 30 weight%, particularly preferably 90 - 40 weight%.

In this case, when blended amount of polypropylene resin is more than 95 weight%, the flexibility and transparency of film and sheet decreases, in addition under 20 weight%, intensity of multilayer laminate which is acquired and moldability of the composition decrease.

In addition, blended amount of polypropylene resin in resin composition (d) of this invention is 100 - 50 weight%, preferably 95 - 80 weight%, particularly preferably 95 - 85 weight%.

In this case, blended amount of polypropylene resin under 50 weight%, is superior in transparency of initial stage of film and sheet, but decrease of the timewise transparency becomes large.

[0006]

Next, hydrogenated diene-based polymer which is used resin composition (a) and as (b) component of the resin composition (d) consists of polymer of at least 1 kind which polymer (below, "hydrogenated prepolymerization body" with you say) which designates random copolymer portion of conjugated diene compound and aromatic vinyl compound as main component hydrogenated is done.

Content of random copolymer portion in hydrogenated prepolymerization body preferably 50 weight% or more, furthermore, is the preferably 60 weight% or more, particularly preferably 70 weight% or more.

In this case, content of said random copolymer portion under 50 weight%, is a tendency where transparency, flexibility, cold resistance, etc., of multilayer laminate which is acquired decreases.

1 and 2 - connection of conjugated diene unit in random copolymer portion and 3 and 4 - ratio of total of connection preferably 60% or more, furthermore, is preferably 65% or more, particularly preferably 70% or more vis-à-vis all conjugated diene unit, in addition, in hydrogenated prepolymerization body.

In this case, description above 1 and 2 - connection and 3 and 4 -ratio of total of connection under 60%, polypropylene resin (J2) with is a tendency where transparency when it blended and improvement effect for flexibility decrease.

In hydrogenated prepolymerization body, as conjugated diene compound, you can list, for example, 1,3- butadiene, isoprene, 2,3-dimethyl-1,3-butadiene, 1,3-pentadiene, 2-methyl-1,3-pentadiene, 1,3-hexadiene, 4,5-diethyl-1,3-octadiene, 3-butyl-1,3-octadiene, chloroprene, etc., but be able to utilize in industrially, to obtain hydrogenated diene-based polymer where in addition property is superior 1 and 3 -butadiene, isoprene, 1,3-pentadiene are desirable, it is a particularly preferably 1,3-butadiene, isoprene.

Mixing alone or 2 kinds or more, you can use these conjugated diene.

In addition, you can list, for example, styrene, α-methylstyrene, p-methylstyrene, t-butyl styrene, divinyl benzene, N,N-dimethyl-p-aminoethyl styrene, N,N- diethyl-p- aminoethyl styrene, vinyl pyridine, etc.., as aromatic vinyl compound, the preferably styrene, α-methylstyrene are.

Mixing alone or 2 kinds or more, you can use these aromatic vinyl compound.

Weight ratio of conjugated diene compound/aromatic vinyl compound in hydrogenated prepolymerization body is not something which especially is limited. preferably 95/5 - 40/60, furthermore, it is a preferably 93/7 - 50/50.

[0007]

Hydrogenated prepolymerization body is something which designates random copolymer portion of conjugated diene compound and aromatic vinyl compound as main component, but from when, below-mentioned or other polymer block may be included in its polymer molecular chain.

As aforementioned polymer block, polybutadiene block, conjugated diene compound which designates homopolymer block, 1, 4- connection of, for example, aromatic vinyl compound as main component and it consists of aromatic vinyl compound and tapered shape polymer block, etc., which crescendo is done it can list aromatic vinyl compound unit.

As for feature on property of hydrogenated diene-based polymer although it decreases somewhat, because handling property improves due to fact that blocking property decreases, there are times when it becomes profitable in industrially due to fact that these polymer block exist in molecular chain of hydrogenated prepolymerization body.

Content of aforementioned polymer block in hydrogenated prepolymerization body is not limited especially. preferably 50 weight% or less, furthermore, it is a preferably 40 weight% or less, particularly preferably 30 weight% or less.

In this case, when content of polymer block exceeds 50 weight%, there is a tendency where transparency, flexibility, cold resistance, etc., of multilayer laminate which is acquired decreases.

[0008]

In addition, hydrogenated prepolymerization body, polymer molecular chain through coupling agent residue, extension or can also possess structure which branch is done.

In this case you can list, for example, diethyl adipate, divinyl benzene, dimethylchlorosilane, tetrachlorosilane, butyl trichlorosilicon, dimethyldichlorosilane, tetrachloro tin, butyl trichloro tin, tetrachloro germanium, 1,2-dibromoethane, 1,4-chloromethyl benzene and bis (trichlorosilyl) ethane, epoxidized linseed oil, toluene diisocyanate, 1,2,4-benzene triisocyanate, etc., as coupling agent which is used.

[0009]

As for hydrogenated diene-based polymer, double bond of conjugated diene portion in hydrogenated prepolymerization body is something which hydrogenated is done.

In case of this hydrogenated, mixing alone or 2 kinds or more, you can use hydrogenated prepolymerization body.

Hydrogenation ratio in hydrogenated diene-based polymer preferably 80% or more, furthermore, is preferably 85% or more, particularly preferably 90% or more.

In this case, when hydrogenation ratio is under 80%, there is a tendency where the transparency, mechanical strength, heat resistance, antiweathering agent, etc., of multilayer laminate decreases.

Number average molecular weight based on polystyrene (below, "number-average molecular weight" with you briefly describe) of hydrogenated diene-based polymer preferably 50, 000 - 700,000, furthermore, is preferably 50,000 - 600,000.

In this case, number-average molecular weight under 50, 000, when pelletizing it does the hydrogenated diene-based polymer, blocking becomes easy to do, at same time when polypropylene resin (J2) with it blended, mechanical strength decreases, in addition when it exceeds 700,000, flow property, fabricability, etc., decreases.

It can produce hydrogenated diene-based polymer, with method which is disclosed in the, for example, Japan Unexamined Patent Publication Hei 3- 72512 disclosure.

[0010]

Furthermore, hydrogenated diene-based polymer which is used resin composition (a) and as (b) component of resin composition (d) can also be modified resin which introduces functional group of one kind or more.

As aforementioned functional group,, for example, carboxyl group, acid anhydride group, hydroxy group, epoxy group, amino group, ammonium salt group, halogen atom-containing basis and sulfonic acid group, etc., and you can list group,, for example, ester group, etc., which is induced from these functional group.

This kind of functional group is introduced before or after hydrogenated for the hydrogenated prepolymerization body according to those types.

Regarding to this invention, mixing alone or 2 kinds or more, you can use the aforementioned hydrogenated diene-based polymer.

[0011]

Resin composition (a) which forms substrate layer of this invention consists of the aforementioned (J2) component and (b) component.

Blended amount of (b) component in said resin composition is 5 - 80 weight%, preferably 10 - 70 weight%, particularly preferably 10 - 60 weight%.

In this case, when blended amount of (b) component decreases, under 5 weight%, flexibility and transparency of film and sheet in addition is more than 80 weight%, intensity and moldability of multilayer laminate which is acquired decrease.

In addition, resin composition (d) which forms surface layer of this invention consists of (b) component which is combined from aforementioned (J2) component and when.

If blended amount of (b) component in said resin composition should have been 50 weight% or less, it is a preferably 5 - 20 weight%, particularly preferably 5 - 15 weight%.

In this case, when blended amount of (b) component exceeds 50 weight%, the initial stage transparency of film and sheet is satisfactory, but decrease of the timewise transparency becomes large.

However, regarding to this invention, it designates blended amount of (b) component in resin composition (d), as below equality to blended amount of (b) component in resin composition (a), it is desirable.

Laminating surface layer which is formed to aspect of at least one of the substrate layer which is formed from resin composition (a), from resin composition (d), being something which becomes, substrate layer and surface layer supply multilayer laminate of this invention, mutually regarding this multilayer laminate, or synergism do, multilayer laminate which possesses characteristic which is superior is formed.

Therefore regarding to this invention, resin composition (a) and blended amount or other condition of combination and (b) component with (J2) component and (b) component in the resin composition (d) are selected appropriately according to desired characteristic of the multilayer laminate.

Regarding to this invention, in range which does not impair feature of this invention essentially, according to need ethylene-propylene copolymer (EPM), ethylene-butene-1 copolymer (EBM), ethylene-propylene-unconjugated diene copolymer (EPDM), polybutene-1, polyethylene or other olefin (co) polymer; ionomer, ethylene-vinyl acetate copolymer (EVA), polyvinyl alcohol (PVA), it is possible also to combine ethylene-vinyl alcohol copolymer (EVOH) or other resin, in resin composition (a) and/or resin composition (d).

In addition, in range which does not impair feature of the this invention essentially, other than according to need antiblocking agent, antistatic agent, lubricant, is possible also fact that organic type antibiotic, inorganic type antibiotic, antioxidant, antifog agent, colorant, ultraviolet absorber or other known additive is combined to resin composition (a) and/or resin composition (d) .

As aforementioned antiblocking agent, for example, silica, zeolite, etc., being ideal, these are good with whichever of natural, synthesis.

In addition which possesses alkyl group of carbon number 12 - 18 as the aforementioned antistatic agent, N,N-bis-(2-hydroxyethyl)-alkyl amines and glycerin fatty acid ester is desirable.

Furthermore, fatty acid amide is desirable as aforementioned lubricant, can list erucic (cis-13 docosenoic) acid amide, behenic acid amide, stearamide, oleic acid amide, etc., concretely.

[0012]

Resin composition of this invention (a) and it mixes with (J2) component and (b) component in resin composition (d), making use of, for example, Banbury mixer, roll mill, extrusion molding machine or other appropriate mixer, it is possible, but melt mixing it does in extrusion molding machine, it is desirable, melt mixing it does making use of especially dual shaft extrusion molding machine it is desirable.

This way fisheye in film and sheet decreases is done with dual shaft extrusion molding machine by using resin composition which melt mixing, not only being superior transparency furthermore, film and sheet which are superior is acquired in external appearance.

Furthermore, resin composition which melt mixing is done, usually, pelletizing doing, is used making use of dual shaft extrusion molding machine.

As for multilayer laminate of this invention,, for example, (a) substrate layer and surface layer after with inflation

method, T-die method or other conventional method forming in film or sheet, heat method of pasting together. Method laminate molding of doing directly with inflation molding machine and T-die extrusion molding machine of(b) coextrusion type. On aspect of at least one of substrate layer or surface layer which formed beforehand with method of (c), for example, aforementioned (a) extrusion is laminated, laminating layer of other with method or other known method which it can produce.

T-die of T-die extrusion molding machine which is used for method of the aforementioned (a) and (b) is good with whichever of multi manifold type or the feed block type.

Among these method, method of (b) is desirable, especially preferred method is method which uses T-die extrusion molding machine of coextrusion type.

With method of aforementioned (b), other than 3 layers coextrusion method which laminate surface layer in both surfaces of 2 layers coextrusion method, substrate layer which laminate surface layer in one surface of substrate layer, multilayer extrusion method of 4 layers or more can be adopted, but from point of change over time of antiblocking property and transparency, surface layer is laminated at least in both surfaces of substrate layer is desirable.

In addition, multilayer laminate of this invention as both mirror surface is used for the application where transparency is required, but with application where transparency is not that much required, it is possible to administer mat, aperture, embossing or other design to at least one of surface layer of outermost layer.

As for multilayer laminate, surface layer is laminated to one surface or both surfaces of substrate layer, but each surface layer which is laminated to both surfaces of substrate layer to one surface or both surfaces of identical or different, and substrate layer, 2 layers or more can also laminate surface layer. this invention

multilayer laminate of this invention can also use, compared to when 2 or more doing to paste together.

Thickness of multilayer laminate of this invention is selected appropriately according to desired characteristic and application of multilayer laminate, but from viewpoint of moldability and intensity, they are 10 μm or greater, it is desirable, furthermore, it is a preferably 20 μm or greater.

In addition, ratio of thickness of substrate layer and surface layer in the multilayer laminate of this invention is selected appropriately according to desired characteristic and application of multilayer laminate, but it is desirable to be a range of the substrate layer/surface layer = 1/1 - 8/1, furthermore, it is a range of preferably substrate layer/surface layer = 2/1 - 6/1.

[0013]

[Embodiment of the Invention]

Below, listing Working Example, furthermore, you explain form of execution of this invention concretely, but if this invention does not exceed gist, it is not something which what constraint is done in these Working Example.

It did various evaluation in Working Example and Comparative Example, following way.

bound amount of aromatic vinyl compound (weight%)

It measured with infrared analysis method due to absorption of phenyl group of 679 cm^{-1}.

Vinyl bond content of conjugated diene portion (%)

It calculated making use of infrared analysis method, with Hampton method.

hydrogenation ratio (%)

Making use of tetrachloro ethylene as solvent, with 100 MHz it calculated with ^{1}H-NMR spectrum.

Number-average molecular weight of hydrogenated diene-based polymer

Calculation based on polystyrene doing with gel permeation chromatography (GPC) in 135°C making use of trichloro benzene as solvent, it calculated.

Film intensity

Conforming to ASTM D882, it measured film intensity, decided with standard below.

Film strength 300 kgf/cm^2 or greater	***	0
film intensity under of 300 kgf/cm^2	***	X
Transparency		

It measured haze (%), decided with standard below. {in case of thickness 40 μm film }		
Haze 2% or lower	***	0
Haze is higher than 2% 3% or lower	***	△
Where haze is higher than 3% {in case of thickness 100 μm film }		X
Haze 3% or lower	***	0
Haze is higher than 3% and lower than 4%	***	△
Haze than 4% higher	***	X
Flexibility		

It measured, decided with standard below.

Young's modulus or less of 30 kg/mm<SP>2</SP>	***	0
Young's modulus is higher than 30 kg/mm<SP>2</SP> *** of 40 kg/mm<SP>2</SP> or less		△
Young's modulus than 40 kg/mm<SP>2</SP> higher	***	X

Cold resistance		
-10°C it decided with standard below with feel in.		
Being a softening equally to case of ambient temperature, it is	***	0
In case of ambient temperature comparing, a little hard	***	△
In case of ambient temperature comparing, very hard		***X
Weld seal strength		

So it decided.

It does not destroy seal and non- seal extends	***	0
It can tear seal, but there is a resistance and also non- seal extends	***	△
There is not a resistance and seal tears	***	X

Change in transparency over time

In constant temperature tank of 50°C 1 week after leaving, film haze (%), conforming to ASTM D 1003, it measured, evaluation did with standard below.

Difference of initial stage haze 0.5 or less						***	0
Difference of initial stage haze is larger than 0.5 1.0 or below * * *							Δ
initial stage	Difference of haze than 1.0 larger					***	X

Each component which is used for combination formulation of Working Example and Comparative Example is as follows.

(J2) component

(E1) polypropylene (Chisso Petrochemical Ltd. manufacture and trade name FM8 31 B)

(E2) polypropylene (Mitsubishi Chemical Corporation (DB 69-056-6740) manufacture, trade name FX4)

(b) Component

Hydrogenated diene-based polymer which is shown in Table 1 (low 1) - (low 6) was synthesized.

Hydrogenated diene-based polymer (low 7) is shell Ltd. supplied hydrogenated styrene-butadiene-styrene block copolymer (SEBS) (trade name Kryton G-1652) .

Collecting microstructure, number-average molecular weight and hydrogenation ratio of these hydrogenated diene-based polymer, to Table 1, it shows.

[0014]

[Working Example(s)]

Working Example 1

Melt mixing after doing, pelletizing it did (E1) component 80 parts by weight and (low 1) component 20 parts by weight, making use of Ikegai Corporation manufacture dual shaft extrusion molding machine PCM-45, acquired resin composition (a) .

In addition, to similar melt mixing after doing, silica 0. 2 parts by weight pelletizing was done as (E1) component 92.5 parts by weight, (low 1) component 7.5 parts by weight and antiblocking agent, resin composition (d) was acquired.

Trilayer film which has feed block equipped T-die supplied each resin composition which it acquires, to moldable extrusion molding machine (For Modern Machinery supplied, substrate layer: for 65 mm diameter, surface layer: 50 mm diameter), 3 layers coextrusion were done as extrusion temperature 240°C, cooling roll temperature 20°C, the ratio of thickness of thickness 40 μm, each layer acquired 3 layers laminate of 1/4/1.

Next, after doing conventional edging, various evaluation were done.

As a result, as for 3 layers laminate which are acquired transparency, flexibility, cold resistance, weld seal strength and film intensity are superior those where in addition also change in transparency over time quite is small.

evaluation result is shown in Table 2.

[0015]

Working Example 2

Other than using (E2) component in place of (E1) component, various evaluation were done to similar to Working Example 1.

As a result, as for 3 layers laminate which are acquired, transparency, flexibility, cold resistance, weld seal strength and the film intensity are superior those where in addition also change over time of the transparency quite is small.

Evaluation result is shown in Table 2.

[0016]

Working Example 3 and Working Example 4

Other than using (B2) component or (B3) component in place of (B1) component, various evaluation were done to similar to Working Example 1.

As a result, as for 3 layers laminate which are acquired, transparency, flexibility, cold resistance, weld seal strength and the film intensity are superior those where in addition also change over time of the transparency quite is small.

evaluation result is shown in Table 2.

[0017]

Working Example 5

To similar to Working Example 1, (E1) component 40 parts by weight and resin composition which consists of(low 1) component 60 parts by weight (a) and (E1) component 85 parts by weight and (low 1) component 15 parts by weight and resin composition (d) which consists of antiblocking agent silica 0.2 parts by weight were acquired.

Next, other than designating thickness as 100 μm, after acquiring 3 layers laminate from each resin composition which is acquired with as similar to Working Example 1, various evaluation were done.

As a result, as for 3 layers laminate which are acquired, transparency, flexibility, cold resistance and the film intensity are superior those where in addition also change over time of the transparency quite is small.

Evaluation result is shown in Table 2.

[0018]

Working Example 6

Resin composition which is similar to Working Example 5 (a) and from resin composition (d), other than ratio of thickness of surface layer and substrate layer acquires 2 layers laminate of 1/4, various evaluation were done to similar to Working Example 1.

As a result, as for 2 layers laminate which are acquired, those where transparency, flexibility, cold resistance and film intensity are superior.

Evaluation result is shown in Table 2.

[0019]

Comparative Example 1 - 4

(B4) - Other than using (B7), various evaluation were done in place of the (B1) to similar to Working Example 1.

As a result, 3 layers laminate of Comparative Example 1, although it is superior in the transparency, weld seal strength and film intensity being inferior change in transparency over time were large, in addition could not use blocking to be extreme as the clothing material packaging film.

Furthermore, 3 layers laminate of Comparative Example 2 - 4 were opaque.

Evaluation result is shown in Table 3.

[0020]

Comparative Example 5

Other than acquiring resin composition (a) from (E1) component 98 parts by weight and (low 1) component 2 parts by weight, various evaluation were done to similar to Working Example 1.

As a result, as for 3 layers laminate which are acquired, transparency, flexibility, weld seal strength, etc., was inferior.

evaluation result is shown in Table 3.

[0021]

Comparative Example 6

Other than acquiring resin composition (a) from (E1) component 10 parts by weight and (low 1) component 90 parts by weight, various evaluation were done to similar to Working Example 1.

As a result, as for 3 layers laminate which are acquired, film intensity was inferior.

Evaluation result is shown in Table 3.

[0022]

Comparative Example 7

Other than acquiring resin composition (d) from (E1) component 60 parts by weight, (low 1) component 40 parts by weight and the silica 0. 2 parts by weight, various evaluation were done to similar to Working Example 1.

As a result, as for 3 layers laminate which are acquired, change in transparency over time was large.

Evaluation result is shown in Table 3.

[0023]

[Table 1]

[Table 1; Translation]

Hydrogenated diene copolymer	B-1	B-2	B-3	B-4	B-5	B-6	B-7
Hydrogenated coplymer composition							

- Conjugated diene compound							
- Aromatic vinyl compound							
- Random copolymer content (weight%)							
- Ratio of total 1,2 bonds to 3,4 bonds per conjugated diene (*2)							
- Weight ratio of conjugated diene compounds to aromatic vinyl compounds							
Hydrogenation rate (%)							
Mean molecular weight (x 10^4)							

*1 BD: butadiene; ST: styrene

*2 Percentage of total conjugated diene compound in random copolymer portion.

[0024]

[Table 2]

[0025]

[Table 3; Translation]

	Working Examples				
Resin composition (c)					
- (a) compound (weight%)					
- (b) compound (weight%)					
Resin composition (d)					
- (a) compound (weight%)					
- (b) compound (weight%)					
Transparency					
Flexibility					
Cold resistance					
Heat seal strength					
Film strength					
Transparency over time					

[Table 3]

[0026]

[Effects of the Invention]

Multilayer laminate of this invention is superior in transparency, flexibility, cold resistance, weld seal strength, heat seal intensity, etc., furthermore, the change in transparency over time is small, film, stationery packaging film, medical packaging film, medical abolition sack for clothing material packaging film, book cover, electronic circuit formation, can use for ideal in medicine hygienic material, decorative film, surface protection film, stationery, food container or other various field.